Tutorials 5 Thermodynamics 2, 2023/2024

Exercise 18

The phase diagram of Bi and Cd is important in metallurgy. These metals are mutually insoluble (immiscible) as solids. In other words, there is no composition for the solids to form a solid solution. Such behaviour leads to a eutectic phase diagram. The general shape of the phase diagram can be approximated by the usual equation for the freezing point depression. Use the following data:
T_{fus}(Bi) = 544.5 K, T_{fus}(Cd) = 594 K, $\Delta_{fus}H$(Bi) = 10.88 kJ/mol en $\Delta_{fus}H$(Cd) = 6.07 kJ/mol.

a) Construct the phase diagram using the expression for the freezing point depression and determine the location of the eutectic point in an approximation by extrapolating both freezing point depression lines in the phase diagram and calculating the intersection point.

b) Examine the change in phases present if the liquid phase with composition x(Bi) = 0.70 at 550 K is slowly cooled.

c) Determine the composition as well as the relative amounts of the phases of the system for an overall composition z(Bi) = 0.70 at 460 K and at 375 K.

d) Make a sketch of the cooling curve for the mixture at z(Bi) = 0.70 in a temperature-time diagram, assuming that the system is cooled by continuously withdrawing a constant amount of heat.

Exercise 19

In this exercise we study the solubility of a solid (solute B) in a solvent A.

a) Derive the following expression for the solubility of a solute B in terms of the mole fraction x_B as a function of the molar fusion enthalpy $\Delta_{fus}H$ and the molar fusion entropy $\Delta_{fus}S$ of the solute for an ideal solution of B in A (Assume that $\Delta_{fus}H$ and $\Delta_{fus}S$ are independent of the temperature).

$$\ln x_B = \frac{\mu_B^*(s) - \mu_B^*(l)}{RT} = -\frac{\Delta_{fus}H_B}{RT} + \frac{\Delta_{fus}S_B}{R}.$$

Hint: A saturated solution corresponds to an equilibrium situation, so $\mu_B(l) = \mu_B(s) = \mu_B^*(s)$.

b) As an example we take a compound with the mysterious name $7\alpha MNa$, a hormone which suppresses menopausal complaints. The solubility of $7\alpha MNa$ in acetone is $x_B = 0.0429$ at $T = 318.5$ K and $x_B = 0.0171$ at $T = 279.3$ K. Calculate the molar fusion enthalpy and entropy of $7\alpha MNa$.

c) For non-ideal solutions we need to revert to the activity in the expression for $\mu_B(l)$. Examine what the expression will be; use that $a_\mathrm{B}(s) \approx 1$, meaning that we are still dealing with a pure solid B(s).

d) In a measurement, the molar fusion enthalpy and entropy of $7\alpha MNa$ at $T = 318.5$ K turn out to be $\Delta_{fus}H = 18.5$ kJ/mol and $\Delta_{fus}S = 35.0$ J/molK respectively. Calculate the activity coefficient γ_B at that temperature.

Exercise 20

Chiral molecules have two enantiomers, a left (S or L) and a right (R or D) one, which are each others mirror image. In the pharmaceutical industry and related industries, it is often essential that the final product is enantiopure. This is mostly achieved through enantioselective synthesis. If this is not possible or too expensive, crystallization can provide an alternative. A method that is often used is to form a salt of the chiral compound with an enantiopure chiral counter ion. If the counter ion and the crystallization conditions are carefully selected, only one of the two enantiomers of the diastereomeric salt will crystallize. We will examine the *l-s* phase diagram for two different mixtures, *conglomerates* (R- and S- enantiomers

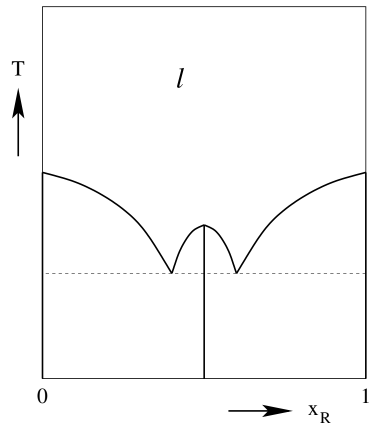

Figure 1: Phase diagram of a racemate.

form separate crystals) and *racemates* (R- and S- enantiomers are present in the same crystal in a 1:1 ratio). We assume that the enantiomers form an ideal solution in the liquid phase.

a) Why is it not possible to separate enantiomers using distillation?

b) Draw the l-s phase diagram of a conglomerate as an x, T diagram at constant pressure.
Hint: look at the result of exercise 18.

In Figure 1 you can find a typical x, T phase diagram for a racemate.

c) Determine which phase can be found where in the diagram and examine what happens if a liquid solution with an initial composition of $x_R \neq 0.5$ is cooled until it is completely solid.

d) Find the conditions (temperature and initial composition) which allow to purify a mixture of enantiomers using crystallization.

Exercise 21

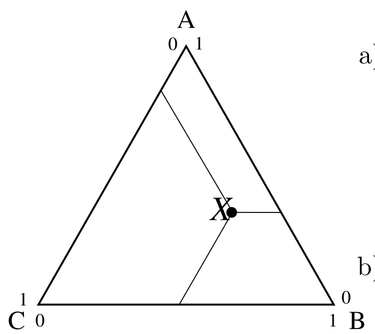

Figure 2: Ternary phase diagram at chosen P and T.

We look back at the situation of exercise 15.

a) Draw the (P, z_A) phase diagram at $T = 90$ °C of the binary mixture of that exercise. The two compounds were *o*-xylene as component A and *m*-xylene as component B. At $T = 90$ °C the pure compound vapour pressures were $P_A^* = 18.5$ kPa and $P_B^* = 21.9$ kPa. Indicate the different phases in the diagram and examine the situation of each region (especially the two-phase region) using Gibbs' phase rule.

b) A ternary phase diagram is often drawn for constant pressure and temperature. In such a diagram, each side of the equilateral triangle represents the mole fraction of one of the three components.
Show that for each point X in such a diagram (like in figure 2) the following equation is valid $x_A + x_B + x_C = 1$, in which the line A, B represents a composition with $x_C = 0$ and analogously for the two other sides.
Hint: this can be done by constructing triangles within the phase diagram.

c) Examine Gibbs' phase rule for this diagram.

d) Draw the results of exercise 15a ($x_A = x_B = 0.5$) and 15e $(x_A, x_B, x_C) = (0.0618, 0.0618, 0.8765)$ in a ternary phase diagram.